A COMPARATIVE STUDY OF THE STRUCTURE & MAGNETIC PROPERTIES OF NICKEL COBALT FERRITES SYNTHESIZED BY SOLID STATE & AUTO-COMBUSTION PROCESSING TECHNIQUES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology in Ceramic Engineering

By
Jyoti Prakash Mallick
Roll no.- 107CR006

DEPARTMENT OF CERAMIC ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA-769008

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Under the guidance of
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NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA
2011

CERTIFICATE

This is to certify that the thesis entitled, **"A COMPARATIVE STUDY OF THE STRUCTURE & MAGNETIC PROPERTIES OF NICKEL COBALT FERRITES SYNTHESIZED BY SOLID STATE & AUTO-COMBUSTION PROCESSING TECHNIQUES"** submitted by **Mr. Jyoti Prakash Mallick** in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

Date: 13/5/2011

Prof. Arun Chowdhury

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Rourkela – 769008

ACKNOWLEDGEMENT

I express my heartfelt gratitude to my guide Prof. Arun Chowdhury for his unflinching support & constant vigil whilst I set about the project. I am ever so thankful to you sir for your co-operation & suggestions without which this project would not have seen the light of day.

I am ingratiated to Prof. B.B.Nayak for helping me in the characterization of the project & Nadiya sir for sitting through the cumbersome process.

I am extremely thankful to Prof. S.K. Pratihar for his guidance & for letting me use the necessary machines as & when required.

I am indebted to my HOD & Faculty Advisor Prof. J.Bera for his help, guidance & support under whom we have prospered.

A warm thank you to all the research scholars especially bhabani bhai, abhishek bhai, geeta di all of whom helped me during the course of my project in different capacities as both mentors & providers.

Last, but not the least, my sincere love to all my friends, Suraj, Alok, Samir, Amit, Akash, Ratre for giving me company while I toiled hard.

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ABSTRACT

Solid state & Auto combustion processing techniques were used to synthesize $Ni_{(1-x)}Co_xFe_2O_4$ where x = 0 to 0.5. In the solid state route, the powders were calcined at 1000^oC for 2hrs, XRD analysis conducted & then each sample sintered at a temperature of 1200^oC & used for magnetic characterization. In the auto combustion synthesis again, the powders were calcined at 1000^oC and then sintered at 1200^oC , XRD analysis of the calcined powder & magnetic characterization of the pellets were carried out. Suitable phases were obtained & the magnetic characterizations were analysed & conclusions were drawn from the available data.

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CHAPTER 1

INTRODUCTION

Ferrites are engineering materials with Fe_2O_3 as their main component. The science of ferrites have their roots in the efforts of many in the early part of the last century. During the 1930s the Philips researchers in Netherlands made important contributions to the science and technology of ferrites; especially the pioneer, J.L. Snoek who saw the industrial significance of ferrites in telecommunications. From the view point of the electrical properties they are semiconductors or insulators, presenting a stark contrast to metallic magnetic materials that are used as electrical conductors. A consequence of it is that the eddy currents produced by alternating magnetic fields are limited in ferrites due to their high intrinsic resistivities. The use of soft ferrites, therefore for high frequency inductors & transformer cores have become prevalent to limit the eddy current loss at high operating frequencies. Besides this, ferrites are also useful in microwave applications, and are also very popular in magneto-optical applications. Hard ferrites however, have high coercivities and high remanence. Strontium ferrites, barium ferrites are examples of it. They also have high magnetic permeability and are used regularly in refrigerator magnets. Ferrite powders are also used to coat magnetic recording tapes. Alnico magnets are used as common radio magnets. Ferro-nano articles also exhibit super-paramagnetic properties with their own array of applications.

Figure 1.1- Soft ferrite components

Range of soft ferrite components:

(i) TV scanning yoke

(ii) UR core and TV line output transformer

(iii) E core for switched mode power supply

(iv) Wide band transformer core

(v) Core giving good magnetic shielding

(vi) High Q filter core

(vii) Precision ferrite antenna for transponder

(viii) Multilayer EMI suppressors

(ix) Toroids for laser and radar pulse applications

(x) Typical EMI shields for cables

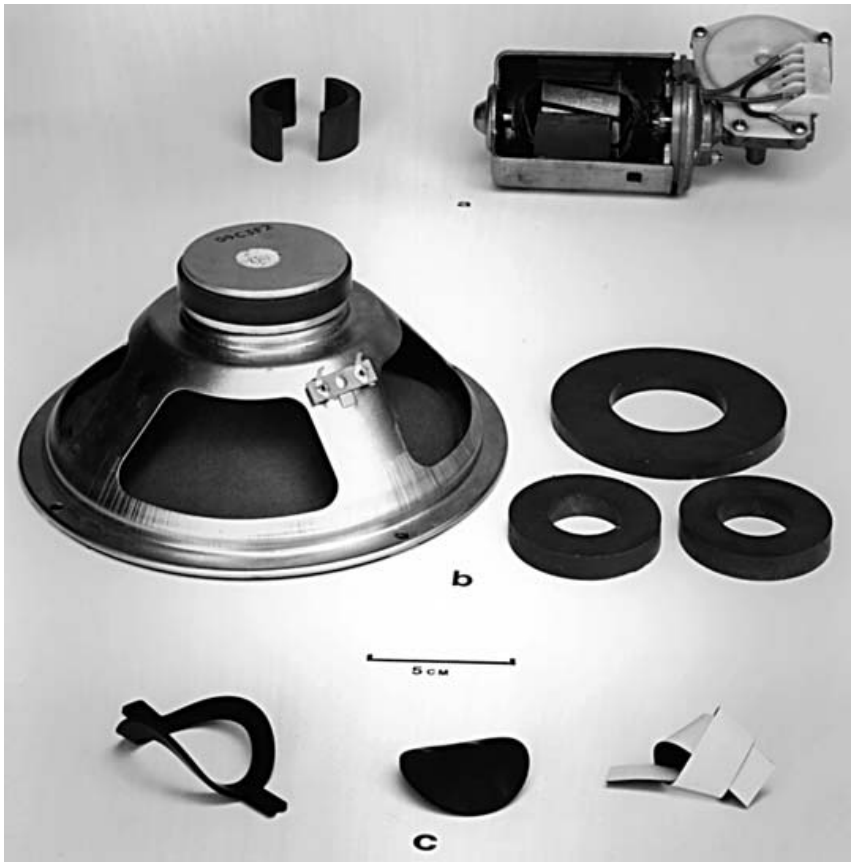


Fig 1.2 Hard ferrite components

(a) Wind screen wiper motor

(b) Loudspeaker and field magnets

(c) Hard ferrite–polymer composite.

NB: The pictures above have been taken from Electro Ceramics by A.J. Moulson & J.M.Herbert.

Nickel ferrite is an example of soft ferrite, spinel ferrites have low magnetic anisotropies and are magnetically ‘soft’, however, Cobalt ferrites which have strong magnetic anisotropy & replaces nickel ions in the octahedral sites as it has the same inverse spinel structure & affects its magnetic properties.

This is an attempt to observe the effect of doping a highly magneto-crystalline anisotropic & magneto-strictive material in a material with very high resistivity i.e. nickel ferrite. Cobalt ion doping causes the pinning of the domain walls due to an increase in anisotropy & has an impact on the magnetic permeability as well as coercivity and saturation magnetization. Two methods have been used for the purpose Solid state & Auto Combustion processing techniques the results so obtained have been studies and conclusions have been made in keeping with the theoretical as well as other published sources.

CHAPTER 2

LITERATURE REVIEW

Nickel ferrite has inverse spinel structure, i.e oxygen ions have cubic closed packing arrangement, Out of the total 64 tetrahedral sites (A sites), 8 are occupied by Fe^{3+} , 8 Ni^{2+} & 8 Fe^{3+} are occupied in 16 octahedral sites(B sites) of a possible 32. There is anti-ferromagnetic coupling between the A & B atoms, & a net magnetic moment is obtained due to the nickel ions. Ni^{2+} has a magnetic moment of 2 μ_B & hence a unit cell of the ferrite has a total magnetic moment of 16 μ_B. Cobalt ferrite also has inverse spinel structure & on adding to the nickel ferrites, it goes into the octahedral sites replacing the Ni^{2+} ions. Co^{2+} has a magnetic moment of 3 μ_B & hence increases the total magnetic moment per unit cell of the nickel cobalt ferrite & it keeps on increasing as we increase Co^{2+} doping in nickel ferrites.

The saturation magnetization of nickel ferrite is given the formula -

$$\mathbf{M_S = 16\ \mu_B / N_a\ a^3}$$

Where M_S = saturation magnetization, μ_B = Bohr magnetron = 9.27 x 10^{-24} A/m^2 , N_a = Avogadro's number, a = lattice parameter.

As we keep on increasing the Co^{2+} doping, there is an increase in the numerator & hence in the saturation magnetization.

An electron, with its orbital magnetic moment & intrinsic spin magnetic moment is free to align itself in any direction with the application of the field. However, due to the spin-orbital lattice coupling restrains most of the directions & only allows the alignment of the spin with relative to the crystal lattice in the minimum energy direction called the 'easy direction' of magnetization. The anisotropy energy ε_k is minimum if the spin is along this 'easy direction'. The anisotropy energy for a cubic lattice is given by-

$$\mathbf{\varepsilon_k = K_1\ (\alpha_1^2\ \alpha_2^2 + \alpha_2^2\ \alpha_3^2 + \alpha_1^2\ \alpha_3^2\ ) + K_2\ \alpha_1^2\ \alpha_2^2\ \alpha_3^2 + \ldots}$$

Where $\boldsymbol{\alpha_1}$, $\boldsymbol{\alpha_2}$, $\boldsymbol{\alpha_3}$ are direction cosines of the magnetization vector relative to the crystallographic axis. The infinite series has negligible terms apart from the first two as shown above, even the second term can be omitted. Assuming that K_2 is negligible & if K_1 is positive, anisotropy energy is minimum if two of the direction cosines are zero. Therefore, the anisotropy energy in this case is minimum along the three crystallographic axes (100), (010), (001) and so on & so forth. Cobalt ferrites is an example of this where cobalt is associated with a high positive anisotropy constant that almost makes it a hard ferrite due to it's high magnetic anisotropy & hence large coercive fields(coercivities of about 10^5 A/m). Nickel ferrite, however, has negative K_1 & hence the easy magnetization direction is the body diagonal (111). Now, we see theoretically the impact that Co^{2+} doping has on the magnetic anisotropy & hence the coercivity of the ferrite, thus putting it in a hard ferrite category from the original soft ferrite **[1].**

X-ray diffraction studies employing the Rietveld analysis was reported on the influence of increasing Co substitution on the structural and micro-structural evolution in AB_2O_4 type spinel ferrites:$Ni_{1-x}Co_xFe_2O_4$ (x = 0.0,0.2,0.4,0.6,0.8and1.0).The specimens have been synthesized by the organic precursor method. Increasing the Co concentrations had the effect of increasing the ratio of [Fe3+]B/[Fe3+]A and gradual expansion of the ferrite unit cell. The microstructure refinement estimated that the particle size values were in the order of nm, ranging from 31 to 61 nm, which gradually increased with increasing Co doping accompanied by almost negligible lattice micro-strains **[2].**

Further Ni-Co ferrites show a good magnetostrictive material, cobalt doping into highly resistive Ni ferrite is one of the important phases for studying of this challenging material. Therefore by keeping this idea in our mind, a study had been conducted **[3]** on the spectroscopic and magnetic

analysis of Ni-Co ferrite with the above mentioned composition prepared by co-precipitation method. It is noticed that saturation magnetization (Ms) and coercivities (H_C) increased with increasing Co*(x).* Similar results were reported by Skomski et al. **[4].**

The decrease in saturation magnetization with increase in Ni content is due to relatively high orbital contribution to the magnetic moment of Co^{2+} ions, which are known to give large induced anisotropy. The coercivity values decreases with increase in Ni content. A decrease in coercivity with increase in Ni content may be attributed to the decrease in anisotropy field, which in turn decreases the domain wall energy **[5].**

Magnetic nano-particles of nickel doped cobalt ferrites have been synthesized by co-precipitation route **[6]**. Both coercivity & saturation magnetization were found to decrease linearly with nickel substitution in cobalt ferrite. A decreasing coercivity may be attributed to to the lower magneto-crystalline isotropy of Ni^{2+} as compared to that of Co^{2+} ions which in turn leads to lower coercivities given by the Stoner-Wolfforth model for nano-particles ($H_C=2K/M_S$) **[7,8].**

A series of cobalt doped nickel ferrite were prepared by using standard ceramic technique **[9]** .B-H measurements were carried out at room temperature under the field of 2.4 kOe & this measurement with the increase in Co^{2+} substitution gave a monotonic increase in the saturation magnetization and a decrease in coercive field at higher cobalt content. Ferrites with such behavior were found to be suitable for magnetic recording media **[10]** . This was explained by the approximate linear dependence of effective anisotropy constant K on composition x in the low Co^{2+} range. In the range of high concentrations, Co^{2+} ions were not considered as isolated & contributions are more complicated. Isolated Co^{2+}- Co^{2+} pairs might have induced a quadratic

dependence of K on composition. This may have been cause the complicated variation of K in the range of higher Co^{2+} concentration.

A series of cobalt doped nickel ferrite with composition of $Ni_{1-X}Co_XFe_2O_4$ with x ranges from 0.0 to 0.8 (in steps of 0.2) were prepared by using co-precipitation method **[11]** .All samples were found to have a cubic spinel structure. TEM had been used to study the resultant morphological variations. The results indicate that the average particle sizes are between 29-35 nm. B-H hysteresis measurement were carried out at room temperature under field of 5 kOe and this measurement with the increase of Co^{2+} concentration yields the monotonic increase of saturation magnetization (M_S) and coercive field (H_C). Ferrites with such behavior have importance in the magnetic recording media, microwave applications, environment and medical biology.

CHAPTER 3

EXPERIMENTAL PROCEDURE

SOLID STATE ROUTE FOR THE SYNTHESIS OF

$Ni_{(1-x)}Co_xFe_2O_{4(x=1-5)}$:

MIXING-

42.488g of Nickel Oxide (NiO) of 72% purity (complexometry based on Ni^{2+}) was weighed out , along with 41.714 of ferric oxide of 98% purity. The weighed chemicals were mixed together. The powder was added to a plastic jar & propan-2-ol was filled in the jar and shaken well. The jar was packed in the pot mill & milled for about 18hrs giving us a homogeneously mixed solution. The solution was placed in a drying oven to remove the moisture & to give us a nickel oxide-ferric oxide powder. The powder along with cobalt oxide (Co_3O_4) acts as raw materials to get nickel cobalt ferrite composites. According to the calculations chalked out, the required weights of cobalt (II,III) oxide & nickel-iron oxide powder were taken for grinding until completely homogenized using propan-2-ol. After carrying out the homogenization process, the paste was left for drying first under air & then under the IR lamp. This process was carried out for all the five compositions of $Ni_{(1-x)}Co_xFe_2O_4$.

CALCINATION- All the 5 samples of different compositions of $Ni_{(1-x)}Co_xFe_2O_4$ ranging from x= 1 to 5 were calcined at 1000^oC for 2 hrs.

The calcined powder was ground in the acetone media to obtain fine powder. XRD analysis was carried out to determine the phases present & purity of the 5 different compositions of nickel cobalt ferrite.

BINDER ADDITION AND PRESSING- The powder samples, five in no., were taken in a mortar. To the power 3% Poly-vinyl alcohol as binder was added and the content was

properly mixed. The powder was then left to dry. After binder addition, 1 samples of 0.72 g each were taken from each of the 5 compositions & were prepared for pressing. The pressure used was of 4 tonnes & the dwelling time taken was 120 secs. The die was cleaned with acetone & lubricated where necessary by stearic acid. Each of the powder samples were then packed in a die and pressed to get a pellet.

SINTERING-

The pellets were subsequently sintered -

- 1 pellet each of 5 different compositions at a temperature of 1200°C for 4hrs in the furnace (OKAY 1700°C) along with a holding time for 1hr at 650°C to account for binder burnout.

  .The pellets (5 in no., 5 different compositions) were then checked for the phases & purity by XRD analysis.

DENSITY MEASUREMENT-

Dry weights of the pellets were taken. The pellets were soaked in kerosene & placed in the vacuum chamber to remove the bubbles. Soaked weights & suspended weights were taken & the experimental densities of the pellets were calculated & compared to the theoretical density.

The pellets were then tested for their magnetic properties by the M-H curve/ Hysteresis loop.

AUTO COMBUSTION ROUTE FOR THE SYNTHESIS OF

$Ni_{(1-x)}Co_xFe_2O_4$ x=1-5): Weighed amounts of Nickel Nitrate hydrate ($Ni(NO3)_2$.6H2O,Source-RANKEM), Cobalt nitrate, Ferric nitrate (Source-MERCK) & Citric acid (Source-MERCK) for all the 5 compositions of nickel cobalt ferrite ($Ni_{(1-x)}Co_xFe_2O_4$). They were taken in separate beakers. To each 100 ml of distilled water was added & the solution was shaken to dissolve the solutes taken. The pH was maintained around 7 by adding ammonia solution. The beaker was then placed on the hot plate with controlled heating & sintering for upto an hour. The gases that come out in the process are H_2O vapors, NO & NO_2. Stirring was stopped & the magnetic needle removed when the solution became viscous. The heating however, was kept on. The evolution of gases increased & finally the dense mass underwent combustion automatically. The beaker was left on the hot plate till it cooled down. The puffed up powder were moved to the mortar & ground till we obtain powder samples. Citric acid, with one hydroxyl & three carboxyl groups is a multi-dentate ligand & complexes with multivalent atoms to form chelates.

CALCINATION-

All the 5 samples of different compositions of $Ni_{(1-x)}Co_xFe_2O_4$ ranging from x= 1 to 5 were calcined at 1000^oC for 2 hrs. The calcined powder was ground in the acetone media to obtain fine powder. XRD analysis was carried out to determine the phases present & purity of the 5 different compositions of nickel cobalt ferrite.

BINDER ADDITION AND PRESSING- The powder samples, five in no., were taken in a mortar. To the power 3% Poly-vinyl alcohol as binder was added and the content was properly mixed. The powder was then left to dry. After binder addition, 2 samples of 0.72 g each were taken from each of the 5 compositions & were prepared for pressing in CARVER press. The pressure used was of 4 tonnes & the dwelling time taken was 120 secs. The die was cleaned with acetone & lubricated where necessary by stearic acid. Each of the powder samples were then packed in a die and pressed to get a pellet.

SINTERING –

The pellets were then fired at a temperature of 1200^{o}C for 4hrs in OKAY furnace (1700^{o}C) accounting for binder burnout by having a holding time of an hour at about 650^{o}C.

The pellets (10 in no., 2 for 5 different compositions) were then checked for the phases & purity by XRD analysis.

DENSITY MEASUREMENT-

Dry weights of the pellets were taken. The pellets were soaked in kerosene & placed in the vacuum chamber to remove the bubbles. Soaked weights & suspended weights were taken & the experimental densities of the pellets were calculated & compared to the theoretical density. The pellets were then tested for their magnetic properties by the M-H curve/ Hysteresis loop.

SOLID STATE ROUTE

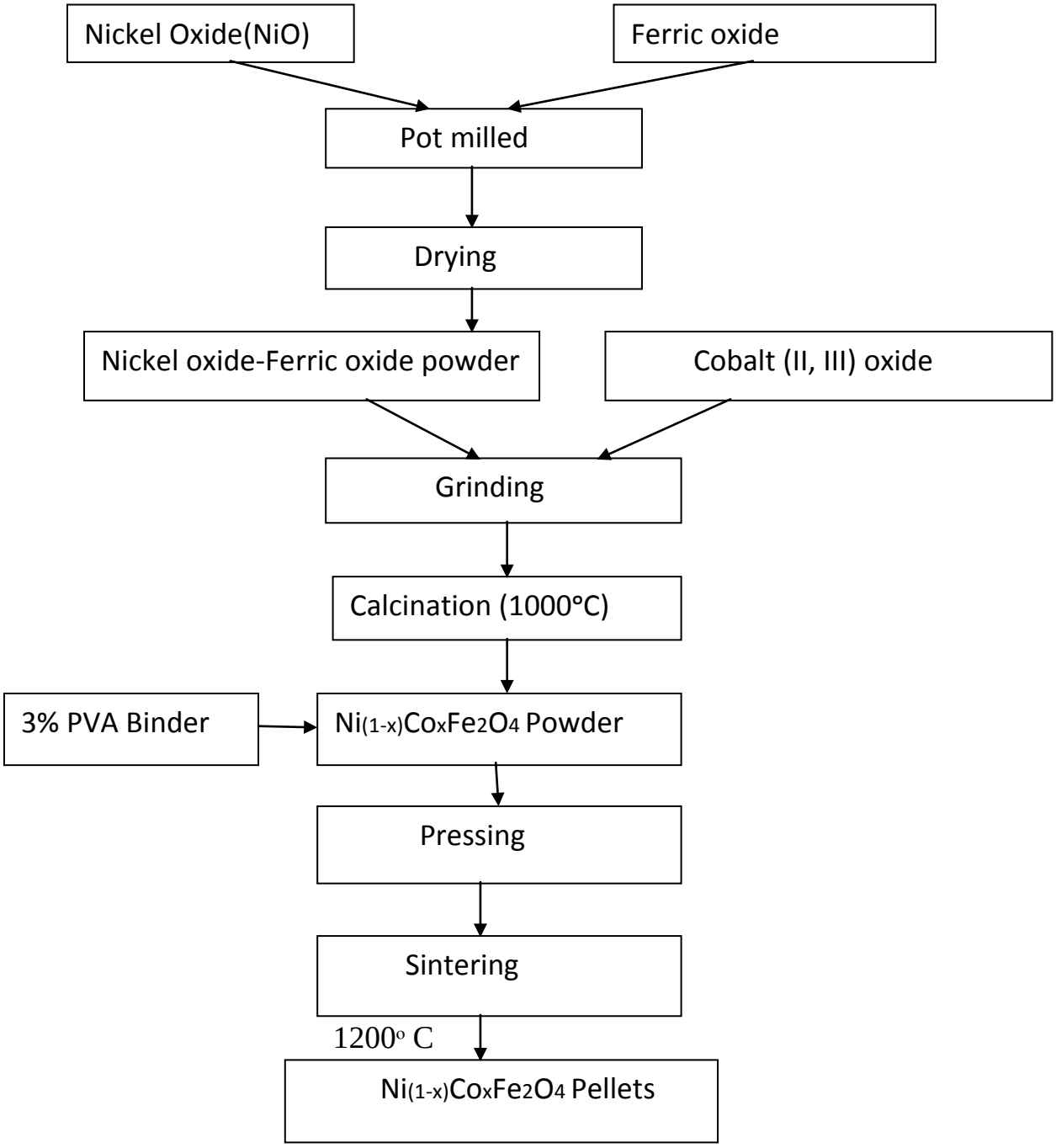


Fig 3.1 – Solid State flowchart

AUTO COMBUSTION FLOW CHART

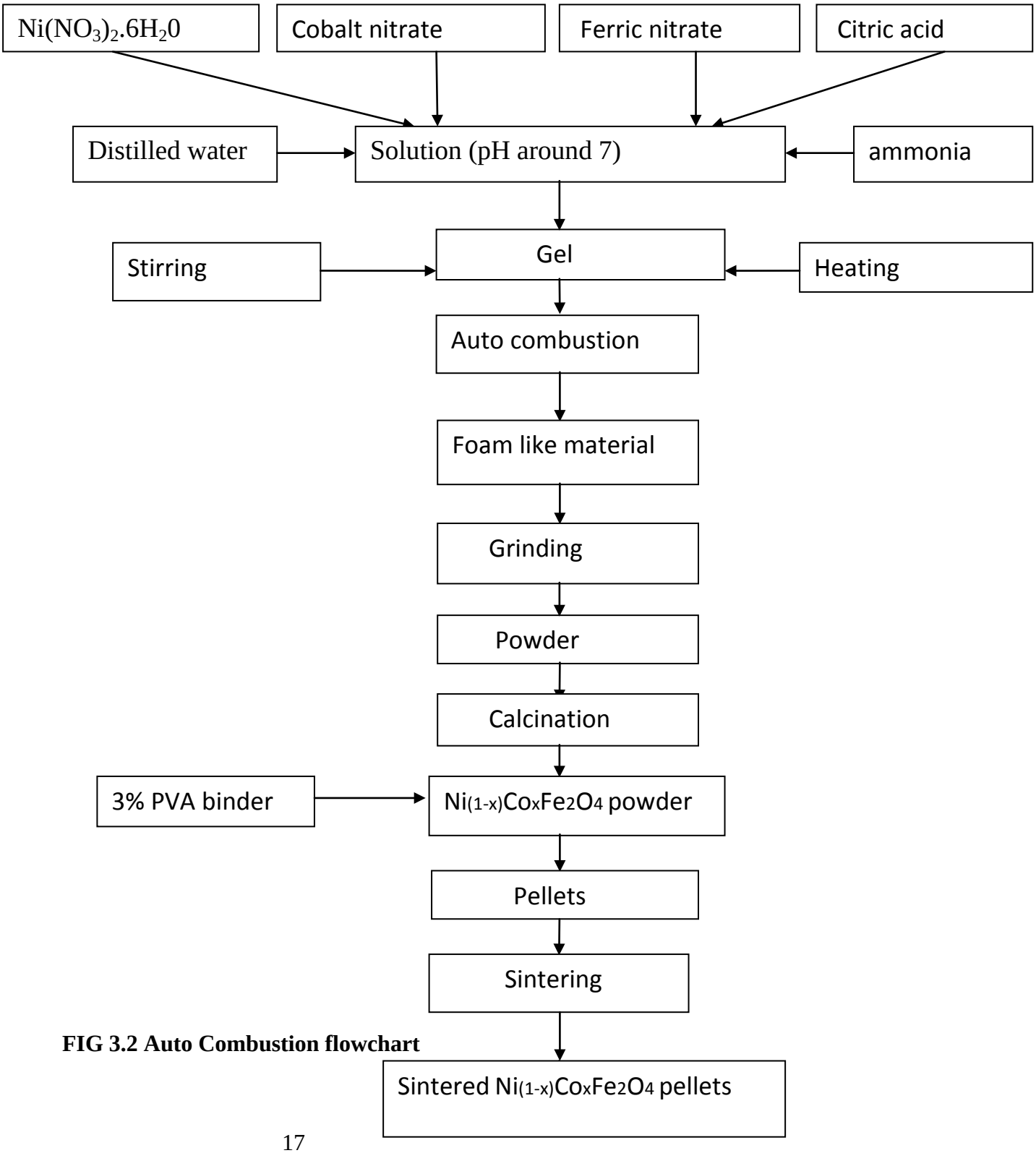


FIG 3.2 Auto Combustion flowchart

CHAPTER 4

RESULTS & DISCUSSIONS

SOLID STATE ROUTE

XRD analysis

X-ray powder diffraction patterns show the presence of nickel ferrite & cobalt ferrite & the peaks completely overlap each other, thus proving that cobalt replaces nickel in the octahedral sites. Some of the legible major peaks are marked as the planes (220), (311),(400), (511), (440) with the diffraction from (311) plane gives the maximum intensity.

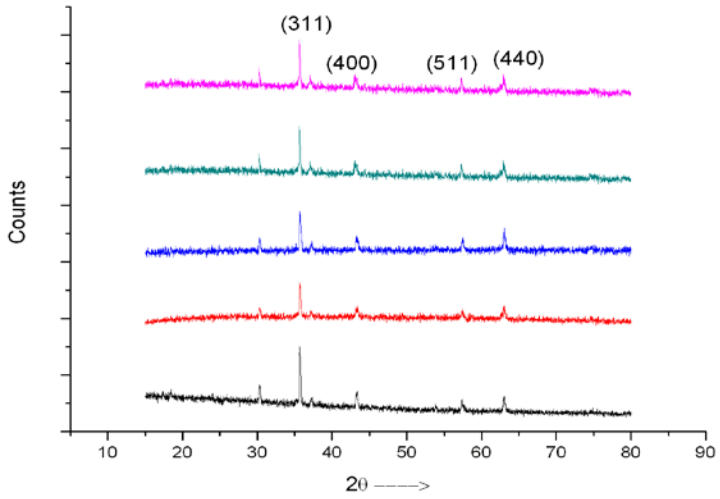


Fig 4.1.1- XRD plots of all the 5 samples

The average particle sizes of the compositions were calculated by the broadening effect given by the Debye-Scherrer's formula for each of the compositions.

$$d = 0.9\lambda / B_{2\theta} \cos \theta$$

where $B_{2\Theta}$ is the full width half maximum in radians, λ the wavelength of the X-ray which is 1.5406 ^{o}A, θ the angle between the incident and diffracted beams and 'd' the particle size of the sample in nm.

Similarly, the lattice parameter can be calculated using the formula

$$\mathbf{a = d_{spacing} * (h^2 + k^2 + l^2)^{0.5}}$$

Composition	Crystallite size(nm)	Lattice parameter
$Ni_{0.9}Co_{0.1}Fe_2O_4$	141.29	8.34313
$Ni_{0.8}Co_{0.2}Fe_2O_4$	169.59	8.34333
$Ni_{0.7}Co_{0.3}Fe_2O_4$	211.99	8.34797
$Ni_{0.6}Co_{0.4}Fe_2O_4$	105.42	8.35666
$Ni_{0.5}Co_{0.5}Fe_2O_4$	129.48	8.35731

Table 1- crystallite size & lattice parameter for the different compositions of nickel cobalt ferrites

Co^{2+} ions have a higher ionic radius of 0.78 A^{o} than $Ni2^{+}$ ions & Fe^{2+} ions, which have an ionic radius of 0.74 A^{o} & 0.67 A^{o} respectively, & hence as we keep on increasing the % of cobalt we have an increase in the lattice parameter from 8.34 ^{o}A to 8.35 ^{o}A.

DENSITY-

Density of Pure cobalt ferrite = 5.29 g/cm^3

Density of Pure nickel ferrite = 5.38 g/cm^3

Table 2 – density table for nickel cobalt ferrite pellets

SAMPLE	DRY WEIGHT IN g	SOAKED WEIGHT IN g	SUSPENDED WEIGHT IN g	EXPERIMENTAL DENSITY	THEORETICAL DENSITY IN g/cm3	% THEORETICAL DENSITY
$Ni_{0.9}Co_{0.1}Fe_2O_4$	0.5638	0.5946	0.4971	4.62	5.371	86.135
$Ni_{0.8}Co_{0.2}Fe_2O_4$	0.5712	0.5978	0.4985	4.60	5.362	85.788
$Ni_{0.7}Co_{0.3}Fe_2O_4$	0.5805	0.6211	0.5162	4.42	5.353	82.570
$Ni_{0.6}Co_{0.4}Fe_2O_4$	0.5563	0.5967	0.4926	4.27	5.344	80.00
$Ni_{0.5}Co_{0.5}Fe_2O_4$	0.5647	0.5985	0.5013	4.64	5.335	87.117

Average bulk density of the pellets of all compositions = 84.322 %

MAGNETIC MEASUREMENTS :

Sintered at 1200°C

The magnetization (in emu/g) vs magnetic field strength(in oersted) curves for x= 0 to 0.5 are shown below-

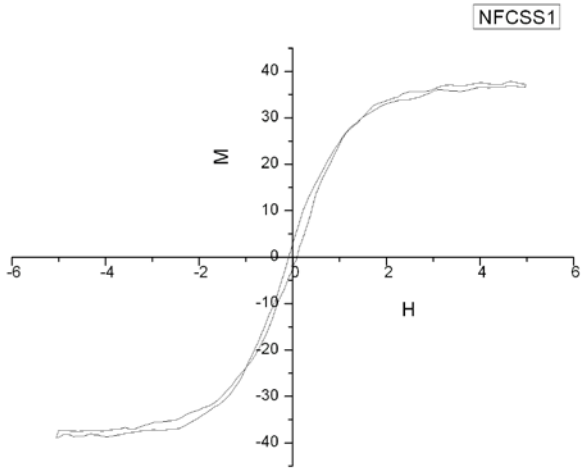


Fig 4.1.2- M-H curve for $Ni_{0.9}Co_{0.1}Fe_2O_4$

M_s = 38.1269 emu/g, H_c = 87.9748 Oe, M_r = 3.3636 emu/g

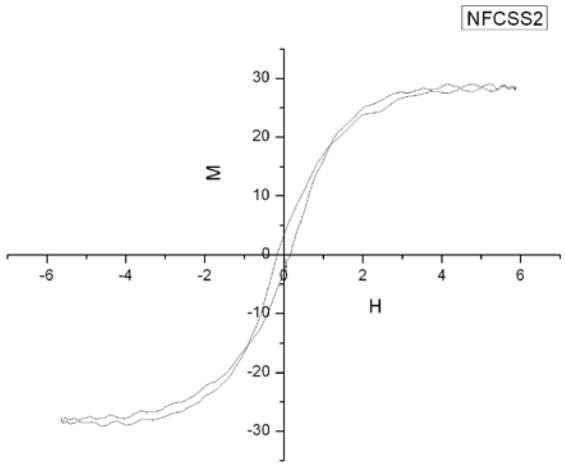


Fig 4.1.3- M-H curve for $Ni_{0.8}Co_{0.2}Fe_2O_4$

M_s = 34.1922 emu/g, H_c = 114.1636 Oe, M_r = 3.8637 emu/g

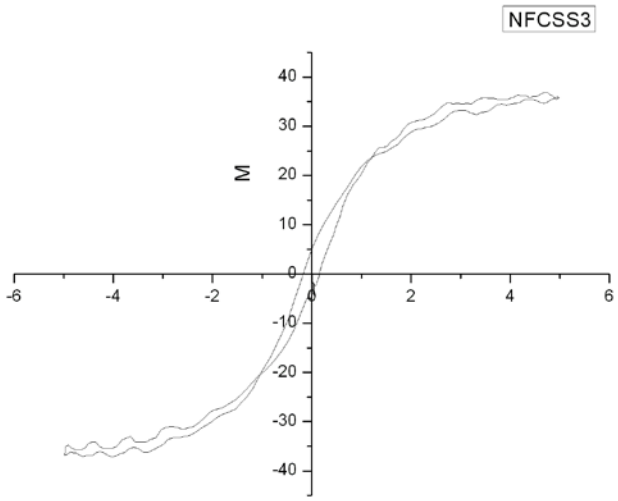


Fig 4.1.4- M-H curve for $Ni_{0.7}Co_{0.3}Fe_2O_4$

M_s = 37.2021 emu/g, H_c = 164.1406 Oe, M_r = 4.012 emu/g

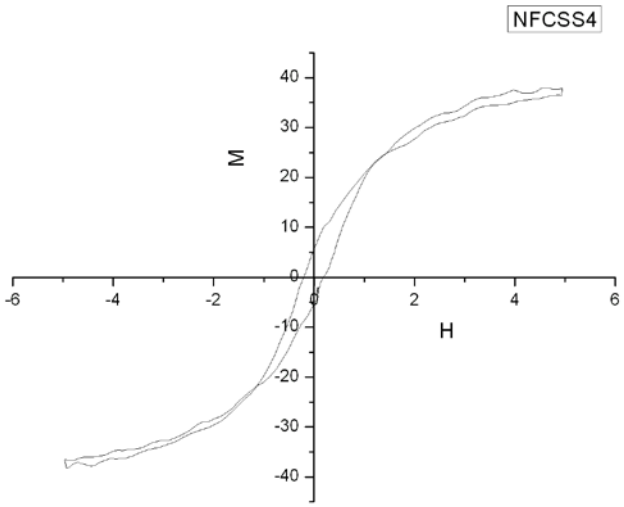


Fig 4.1.5- M-H curve for $Ni_{0.6}Co_{0.4}Fe_2O_4$

M_s = 38.3664 emu/g, H_c = 197.8125 Oe, M_r = 4.1042 emu/g

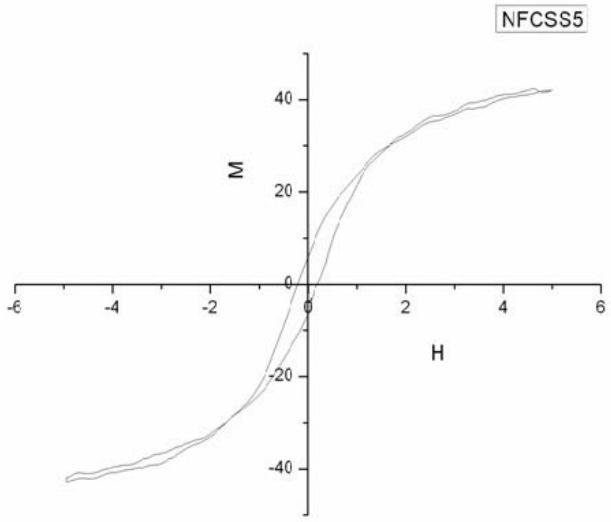


Fig 4.1.6- M-H curve for $Ni_{0.5}Co_{0.5}Fe_2O_4$

M_s = 43.6742 emu/g, H_C = 199.1236 Oe, M_r = 4.6720 emu/g

There will be a dependence on anisotropy constant K on the Co^{2+} concentration by the following relation-

$$K = H_C M_S / 2$$

As Co^{2+} is highly magnetically anistropic which places them in the hard ferrites category, therefore as we keep on increasing the Co^{2+} doping in nickel ferrites, there's a rise in the coercivity as seen from the figure.

However, saturation magnetization values show no specific increase in values, this is due to the solid state route which doesn't yield uniform size distribution of particles. The process parameters are not refined & hence, the slight increase in M_S is not seen in this method.

H_C VS Co Doping

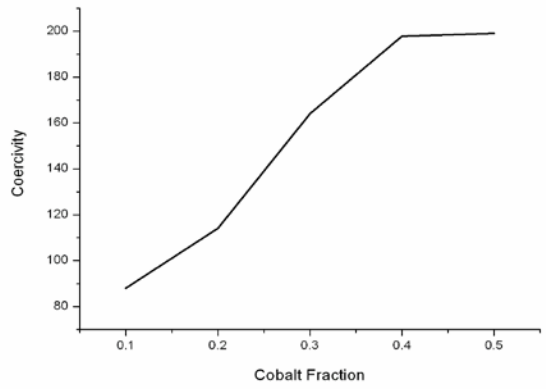


Fig 4.1.7 – coercivity vs cobalt fraction plotted

AUTO COMBUSTION

XRD analysis

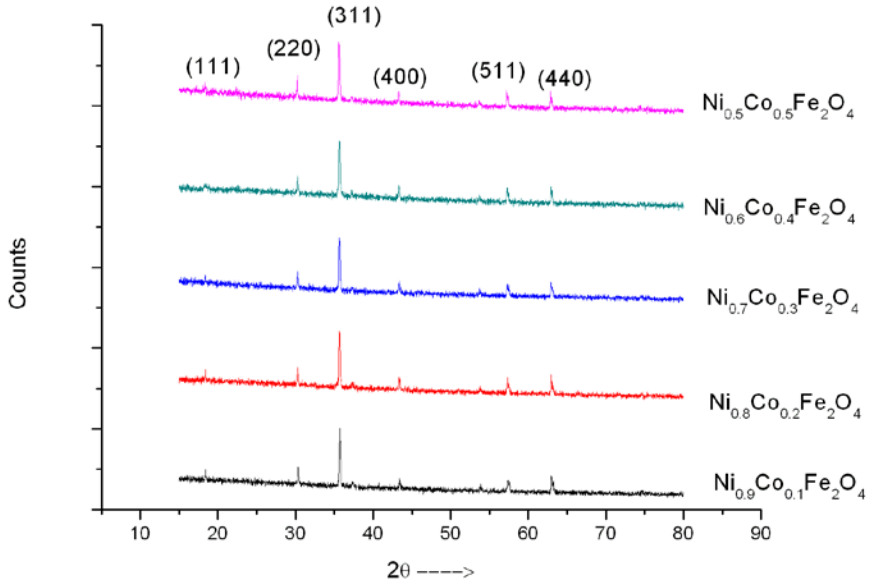


Fig 4.2.1-XRD plots of nickel cobalt ferrites

X-ray powder diffraction patterns show the presence of nickel ferrite & cobalt ferrite & the peaks completely overlap each other, thus proving that cobalt replaces nickel in the octahedral sites. Some of the legible major peaks are marked as the planes (111), (220), (311),(400), (511), (440) with the diffraction from (311) plane gives the maximum intensity at Bragg's angle 2Θ = 35.6786°, 35.6187°, 35.624°, 35.6179°, 35.5795° for x= 1 to 5 respectively. The average particle sizes of the compositions were calculated by the broadening effect given by the Debye-Scherrer's formula for each of the compositions.

$$d = 0.9\lambda / B_{2\theta} \cos\theta$$

where $B_{2\Theta}$ is the full width half maximum in radians, λ the wavelength of the X-ray which is 1.5406 °A, θ the angle between the incident and diffracted beams and 'd' the particle size of the sample in nm.

Similarly, the lattice parameter can be calculated using the formula

$$\mathbf{a = d_{spacing} * (h^2 + k^2 + l^2)^{0.5}}$$

Table 3 – crystallite size & lattice parameter for nickel cobalt ferrites

Composition	Crystallite size(nm)	Lattice parameter
$Ni_{0.9}Co_{0.1}Fe_2O_4$	141.29	8.34641
$Ni_{0.8}Co_{0.2}Fe_2O_4$	121.10	8.35832
$Ni_{0.7}Co_{0.3}Fe_2O_4$	142.32	8.35875
$Ni_{0.6}Co_{0.4}Fe_2O_4$	121.00	8.36041
$Ni_{0.5}Co_{0.5}Fe_2O_4$	169.48	8.36890

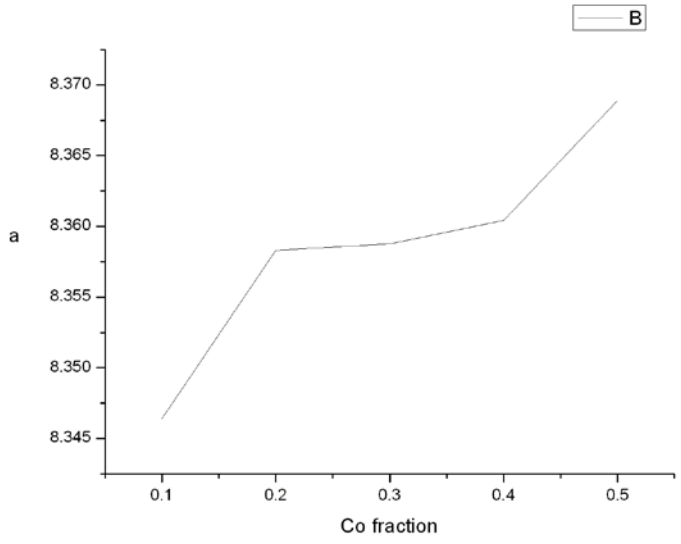


Fig 4.2.2 – lattice parameter vs Co^{2+} fraction

There is a marked increase in the lattice parameter as we increase the Co content in nickel ferrite. This can be attributed to the different ionic radii of the species present in the samples. Co^{2+} ions

have a higher ionic radius of 0.78 A^o than $Ni2^+$ ions & Fe^{2+} ions, which have an ionic radius of 0.74 A^o & 0.67 A^o respectively, & hence as we keep on increasing the % of cobalt we have an increase in the lattice parameter from 8.34641 to 8.36890.

DENSITY-

For the samples produced by **Auto Combustion method**, the pellet densities were calculated & compared with the theoretical densities.

Density of Pure cobalt ferrite = 5.29 g/cm^3

Density of Pure nickel ferrite = 5.38 g/cm^3

Table 4 – density measurements for nickel cobalt ferrite pellets

SAMPLE	DRY WEIGHT IN g	SOAKED WEIGHT IN g	SUSPENDED WEIGHT IN g	EXPERIMENTAL DENSITY	THEORETICAL DENSITY IN g/cm3	% THEORETICAL DENSITY
$NiFe_2O_4$	0.7262	0.7555	0.6374	4.9192	5.38	91.435
$Ni_{0.9}Co_{0.1}Fe_2O_4$	0.6855	0.7054	0.5921	4.8402	5.371	90.117
$Ni_{0.8}Co_{0.2}Fe_2O_4$	0.6597	0.6777	0.5684	4.8285	5.362	90.050
$Ni_{0.7}Co_{0.3}Fe_2O_4$	0.7047	0.7168	0.5982	4.7534	5.353	88.798
$Ni_{0.6}Co_{0.4}Fe_2O_4$	0.7151	0.7239	0.6137	5.1912	5.344	97.140
$Ni_{0.5}Co_{0.5}Fe_2O_4$	0.6745	0.6696	0.5607	4.9550	5.335	92.877

Average bulk density of the pellets of all compositions = 91.736 %

Of the 10 pellets, 2 of each composition the above samples were chosen for XRD analysis & other properties because they had relatively higher densities than the other pellet of the same composition.

Density of kerosene = 0.8 g/cm^3

Density = [dry weight/ (soaked weight – suspended weight)] * 0.8

MAGNETIC MEASUREMENTS

The magnetization (in emu/g) vs magnetic field strength(in oersted) curves for x= 0 to 0.5 are shown below-

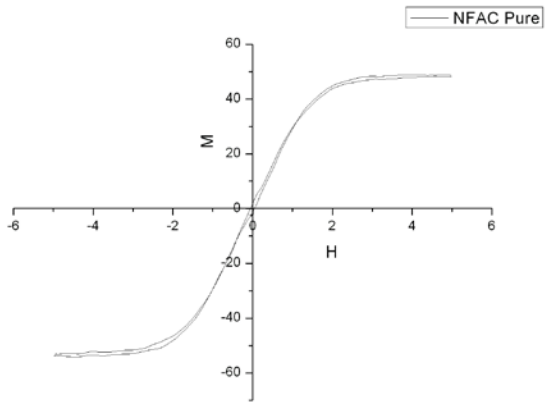


Fig 4.2.3- M-H curve for $NiFe_2O_4$

M_s = 48.9928 emu/g, H_c = 30.8177 Oe, M_r = -5.504 emu/g

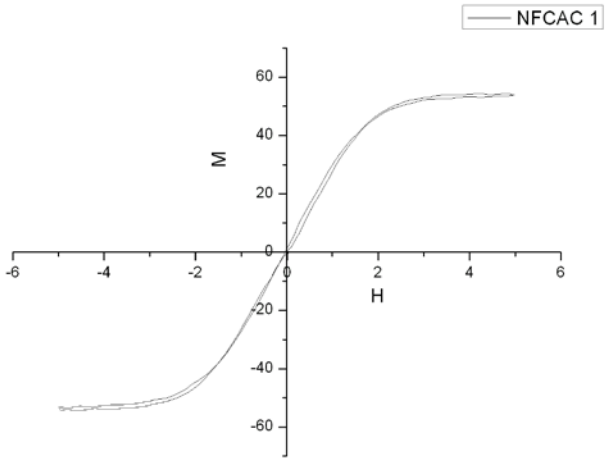


Fig 4.2.4- M-H curve for $Ni_{0.9}Co_{0.1}Fe_2O_4$

M_s = 54.5263 emu/g, H_c = 48.6563 Oe, M_r = 1.1054 emu/g

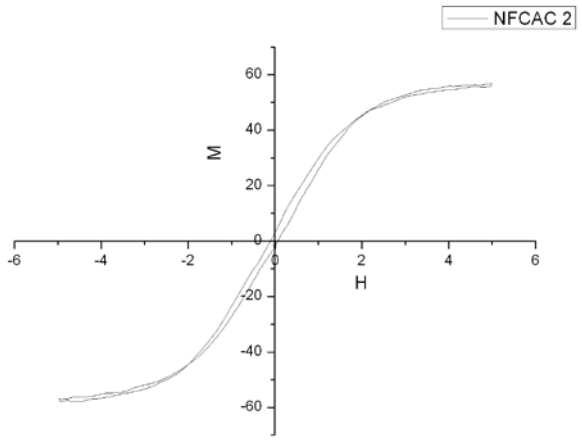


Fig 4.2.5- M-H curve for $Ni_{0.8}Co_{0.2}Fe_2O_4$

M_s = 55.4672 emu/g, H_c = 86.6645 Oe, M_r = 2.366 emu/g

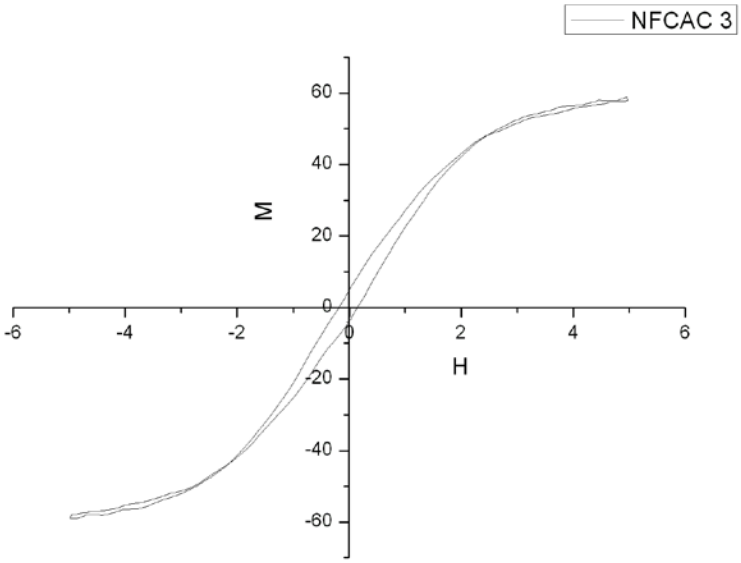


Fig 4.2.6- M-H curve for $Ni_{0.7}Co_{0.3}Fe_2O_4$

M_s = 59.6314 emu/g, H_c = 167.9385 Oe, M_r = 4.0953 emu/g

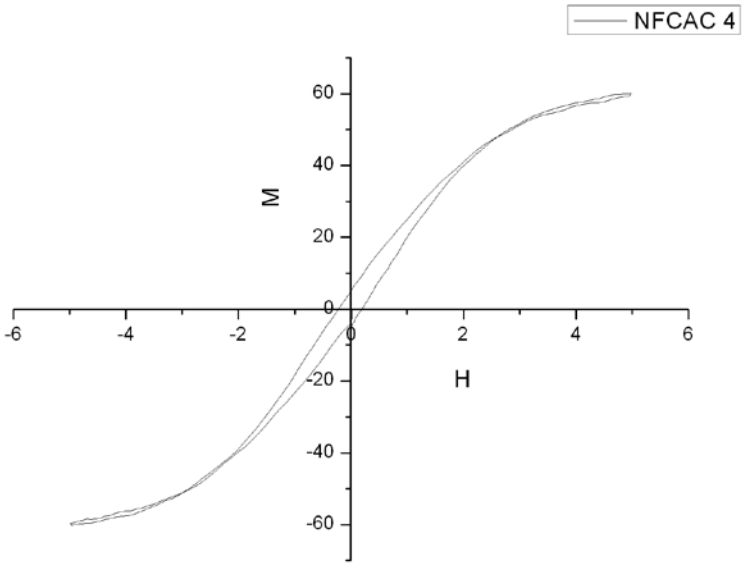


Fig 4.2.7- M-H curve for $Ni_{0.6}Co_{0.4}Fe_2O_4$

M_s = 61.6542 emu/g, H_c = 206.6931 Oe, M_r = 4.7345 emu/g

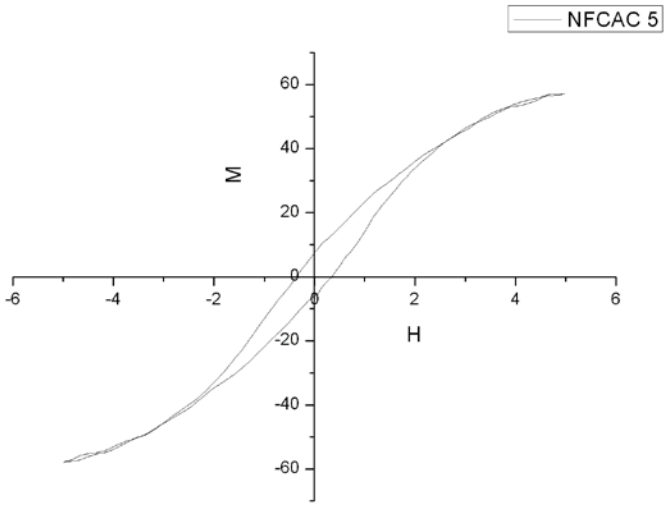


Fig 4.2.8- M-H curve for $Ni_{0.5}Co_{0.5}Fe_2O_4$

M_s = 69.8633 emu/g, H_c = 358.1934 Oe, M_r = 8.3194 emu/g

The plots show a monotonic increase in the saturation magnetization as well as coercivity values on an increase in cobalt doping in the ferrites. This is due to the substitution of nickel in octahedral sites by cobalt. The increasing Co^{2+} content on the octahedral sites leads to an increase in the magnetic moment per formula of $Ni_{1-X}Co_XFe_2O_4$ & hence an enhancement in the magnetization of $Ni_{1-X}Co_XFe_2O_4$.

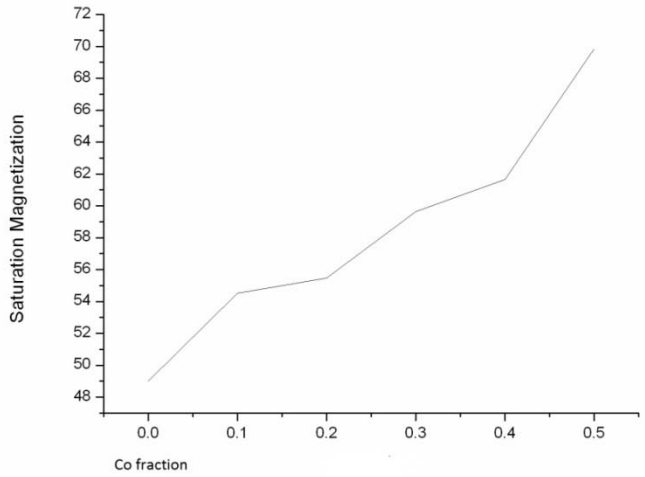
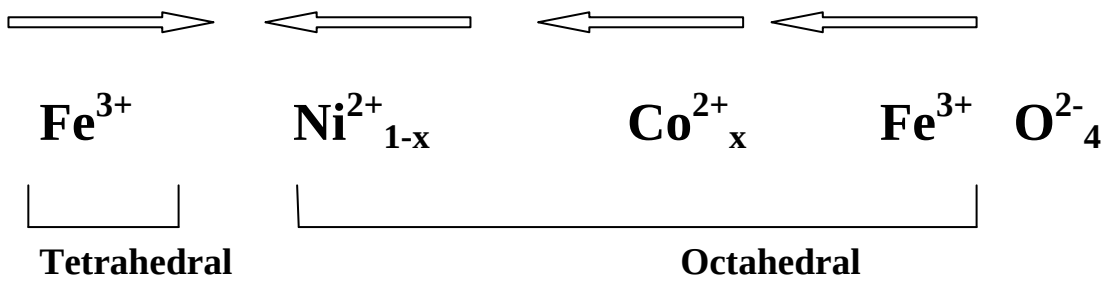


fig 4.2.9 – saturation magnetization vs Co mole fraction doped

The magnetic moment of a Co^{2+} ion is equal to 3 μB, that of Ni^{2+} is 2 μB & for Fe^{3+} the magnetic moment is 5 μB. When x increases this leads to the compensation of Fe^{3+} ions in the tetrahedral & octahedral sites, the shift in the $Ni_{1-X}Co_XFe_2O_4$ structure is shown below-



H_C VS Co Doping

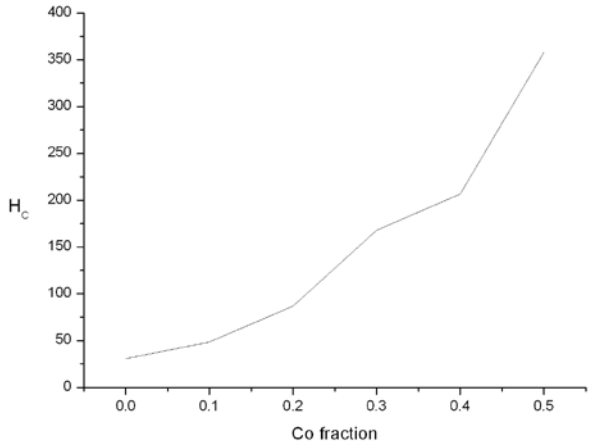


fig 4.2.10 – Coercivity vs Co mole fraction doped

There will be a dependence on anisotropy constant K on the Co^{2+} concentration by the following relation-

$$\mathbf{K = H_C M_S / 2}$$

As Co^{2+} is highly magnetically anistropic which places them in the hard ferrites category, therefore as we keep on increasing the Co^{2+} doping in nickel ferrites, there's a rise in the coercivity as seen from the figure & given by the following relation-

$$\mathbf{H_C = a.\ K_1/M_S + b\ (N_1 - N_2)\ M_S + c\ (\lambda_s \tau / M_S)}$$

Where **a**,**b**,**c** are constants, $\mathbf{N_1}$ & $\mathbf{N_2}$ are demagnetization factors determined along two perpendicular directions, λ_s is the magneto-striction factor & τ the mechanical strain**.**

The first term gives us the magneto-crystalline anisotropy of the material; the second term corresponds to the shape anisotropy of the material, whereas the third term gives the effect of the effect of elastic mechanical deformation. However, it is the first term which is due to the doping of Co^{2+} that gives an increasing trend in the coercivity values.

Table 5 - Magnetic data comparison of solid state & auto combustion routes

SAMPLE	Saturation magnetization(emu/g)		Coercivity (Oe)		Remnant magnetization(emu/g)	
	Solid state	Auto combustion	Solid state	Auto combustion	Solid state	Auto combustion
$Ni_{0.9}Co_{0.1}Fe_2O_4$	38.1269	54.5263	87.9748	48.6563	3.3636	1.1054
$Ni_{0.8}Co_{0.2}Fe_2O_4$	34.1922	55.4672	114.1636	86.6645	3.8637	2.366
$Ni_{0.7}Co_{0.3}Fe_2O_4$	37.2021	59.6314	164.1406	167.9385	4.012	4.0953
$Ni_{0.6}Co_{0.4}Fe_2O_4$	38.3664	61.6542	197.8125	206.6931	4.1042	4.7345
$Ni_{0.5}Co_{0.5}Fe_2O_4$	43.6742	69.8633	199.1236	358.1934	4.6720	8.3194

The observations made from the above table after comparing the data from the solid state and auto combustion processing techniques were-

- For the same composition the ‘Saturation magnetization’ is higher in samples obtained from the auto combustion route.
- Coercivity value is higher in Auto combustion route for addition of 30 mol% of Co and onwards.
- Only the $Ni_{0.5}Co_{0.5}Fe_2O_4$ in auto-combustion sample is having comparatively higher remnant magnetization than it’s counterpart (solid state route).

CONCLUSIONS

- The combustion synthesis is very much advantageous over the solid state synthesis because it gives better compositional homogeneity and purity of the final product; this explains the discrepancies shown by the products synthesized from solid state route. Finer particle size of the ferrite powder is the reason behind the lower sintering temperature of Auto combustion method. This is evident from the comparison of the average density data.

- Ideally, & as shown in the Auto Combustion route, the saturation magnetization increases with Cobalt ion doping; even a discernible, yet non-uniform trend is also seen in the solid state process.

- The coercivity values increase on increased cobalt ion doping owing to the high magneto-crystalline anistropy of cobalt ion.

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